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PROGRESS REPORT NO. 1

June 4, 1955 - March 3, 1956

THE FIRE RESISTANT TREATMENT OF TEXTILES

Headquarters, Quartermaster Research and
Development Command
Quartermaster Research and Development Center
Contract No. DA19-129-qm-324
Project No. 7-97-06-001

Department of Chemistry
University of Rhode Island
Kingston, Rhode Island

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Morton H. Gollis
Frank R. Fisher
Carl H. Stetson, Jr.
Aram Tomasian

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PROGRESS REPORT NO. 1

THE FIRE RESISTANT TREATMENT OF TEXTILES

SUMMARY

The development of organophosphorus compounds as fire retardants for cotton fabrics has continued. Compounds are under investigation that may provide both water-repellency and fire resistance by reaction with cellulose in a manner similar to that believed to be the basis for the durability of the Zelan process.

Kinetic studies of the pyrolysis of untreated and treated cotton fabrics have been discontinued in favor of pure cotton fiber. The purification of a sample of field cotton is in process.

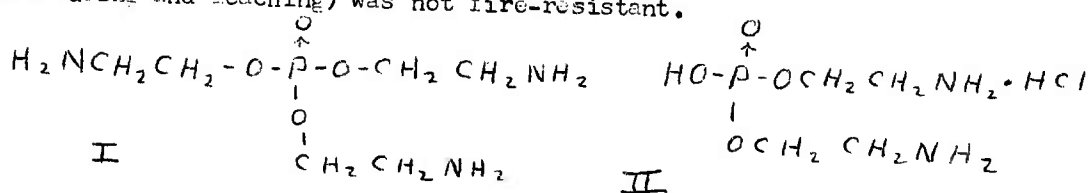
An evaluation program of the radiant energy decomposition of untreated and treated cotton is in progress. This program includes the comparison of char and tar resulting from furnace pyrolysis with that produced by radiant energy decomposition.

RESULTS AND DISCUSSION

Compound Development

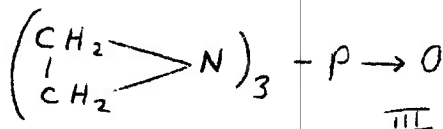
The development and evaluation of organic compounds as fire retardants for cotton fabrics has been continued. As in the past, the emphasis has been directed to organophosphorus compounds, which can be polymerized on the fabric during the curing process to provide a durable treatment.

Di- β -aminoethylphosphoric Acid Monohydrochloride. An earlier progress report from this laboratory¹ stated the possibility of tri- β -aminoethyl phosphate (I) as a fire-retardant treatment. Although this compound could not be prepared, the di-ester, di- β -aminoethylphosphoric acid monohydrochloride (II), was obtained according to the method of Jackson² from the reaction of phosphorus oxychloride and ethanolamine. A slightly alkaline aqueous solution of II and an excess of formaldehyde was applied to cotton khaki fabric. The treated fabric (21.6% add-on after curing and leaching) was not fire-resistant.

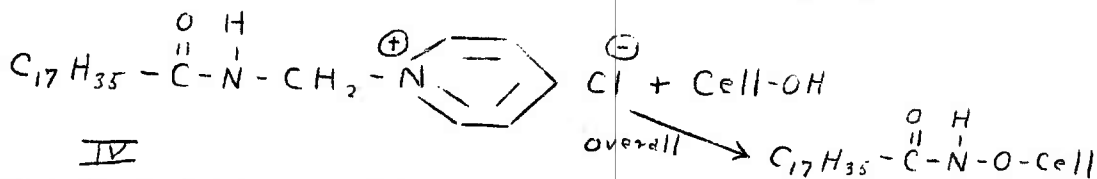


Durability of Treatment by Reaction with Cellulose. Chemical modification has often been considered as a means of imparting permanent fire resistance to cellulosic fabrics. An earlier progress report from this laboratory³ considered that such a modification might be produced by an amide of phosphoric acid, the nitrogen of which was provided by the reactive ethyloneimine group. A simple model of such a compound, N,N',N''-tri-

ethylene phosphoric triamide (III), was prepared and its evaluation started. However, further consideration of such compounds as III has been discontinued because of the report that another laboratory has undertaken a similar study.



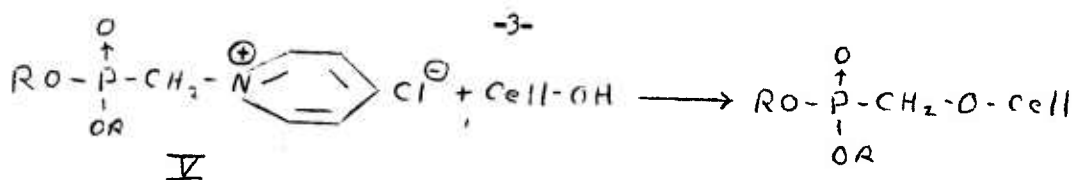
Chemical modification of the hydroxyl groups in cellulose is a means of providing cotton fabrics with durable water-repellency. The compounds which are of greatest commercial importance in providing durable water-repellency to cotton fabrics possess a long chain aliphatic group (n-octadecyl or n-heptadecyl) as the hydrophobic element and a solubilizing quaternary ammonium group. Zelan (IV) is probably the best known compound of this class. The results of various investigations indicated that the durable water-repellency obtained with this compound is caused by etherification of cellulose to produce stearamidomethyl ether groups.



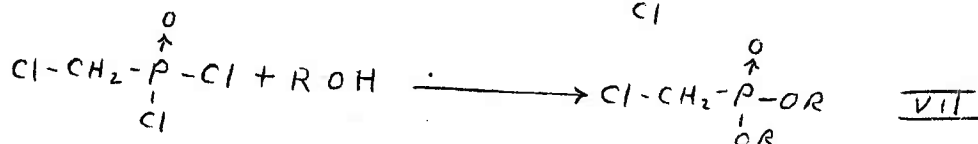
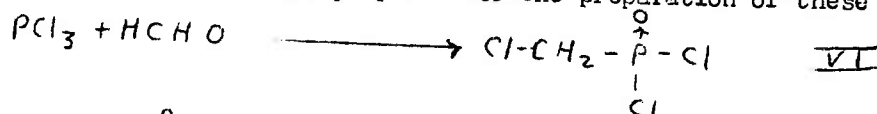
A more detailed summary of the chemical reactions involved in water-repellency treatments using quaternary ammonium salts of the Zelan type is given in a recent publication⁴.

The resistance to laundering and cleaning of such cationic chemical agents as Zelan indicate that the combination of a hydrophobic group (long chain alkyl radical), an element with fire-retardant properties (phosphorus) and a solubilizing (quaternary ammonium) group will produce compounds which may provide effective durable fire-retardant and water-repellent treatments for cotton fabric.

The preparation of compounds of structure V, which will be screened for water-repellent and fire-retardant properties is under investigation.



The following procedure is proposed for the preparation of these compounds:



The preparation of the intermediate compounds VI (chloromethylphosphonyl dichloride) and VII (dialkyl chloromethylphosphonate; R = methyl, ethyl) has been reported by Russian investigators⁵.

Chloromethylphosphonyl dichloride (VI) was prepared according to the procedure of Kabachnik and coworkers⁵ by heating a mixture of phosphorus trichloride (1 mole) and paraformaldehyde (0.67 mole, based on formaldehyde) in a small steel bomb for 20 hours at $200 \pm 5^\circ\text{C}$. The excess phosphorus trichloride was removed from the cooled amber reaction mixture by flash distillation. Distillation of the liquid residue under reduced pressure produced 44.4g. (40%) of the colorless desired product, b.p. 82°C . (12mm.), n_D^{24} 1.4941.

Diethyl chloromethylphosphonate (VII, R = ethyl) was prepared⁵ by the dropwise addition of chloromethylphosphonyl dichloride to an excess of absolute ethyl alcohol with stirring and cooling. The reaction mixture was allowed to increase to room temperature after the addition was completed. After removal of excess alcohol, the liquid residue was fractionated to yield a colorless oil with an ester odor, b.p. $74-77^\circ\text{C}$. (1-2mm.), n_D^{27} 1.4360, in fair yield (41-53%).

As outlined in the reaction scheme, the preparation of diethylphosphonomethylpyridinium chloride (V, R = ethyl) will be investigated by inter-action of diethyl chloromethylphosphonate and pyridine.

Mechanism of the Pyrolytic Decomposition of Cellulose

The study of the pyrolysis rate of cotton fabrics has continued. In Figures 1-4 is given the variation of per cent char with time for some untreated cellulosic fabrics at various temperatures. The decomposition is first-order as shown in Figures 5-8. In Table I is listed the specific rate constants obtained. The enthalpy of activation listed in Table II was obtained in the conventional manner from the slope of the straight line obtained from a graphical plot of the logarithm of the rate constant against the reciprocal of the absolute temperature.

Table III summarizes the first-order specific rate constants in the pyrolysis of cotton khaki twill, treated with inorganic compounds.

The further use of cotton fabric in the study of pyrolysis kinetics has been discontinued. The use of purified cotton, treated and untreated has been adopted. A supply of field cotton has been obtained^a and carded. Purification of this cotton according to the general procedure outlined by Conrad⁶ is in progress. The history of the purification process will be known. The rate of pyrolysis of untreated and treated samples will be studied. In addition, the effect of increasing add-on on the rate will be determined.

TABLE I

Specific Rate Constant (min.⁻¹) Observed in the Pyrolysis of Some Untreated Cellulosic Fabrics at Different Temperatures

Temperature (°C.):	<u>300</u>	<u>308</u>	<u>315</u>	<u>320</u>	<u>325</u>	<u>335</u>	<u>340</u>
Cotton Khaki	.0186		.0363		.0683		.1830
80 sq. Cotton	.0209	.0334		.0768	.0957		
Linen	.0224		.0520		.0883	.1570	.3220
Rayon	.0704		.1930		.3430		

^aThe cotton was obtained through the kind efforts of Dr. Ramon Esteve.

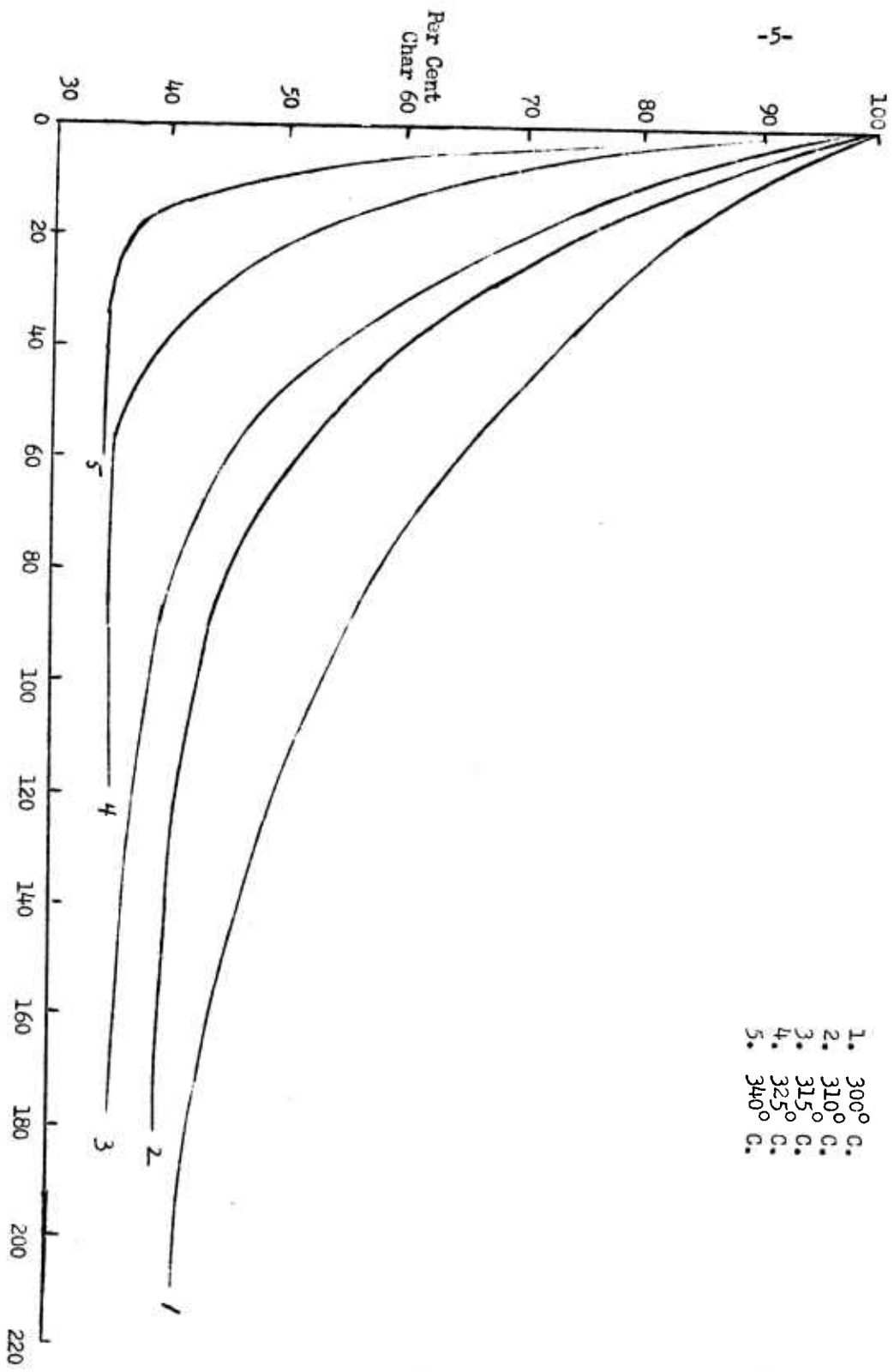


Figure 1. Variation of char with time in the Pyrolysis of untreated cotton khaki fabric

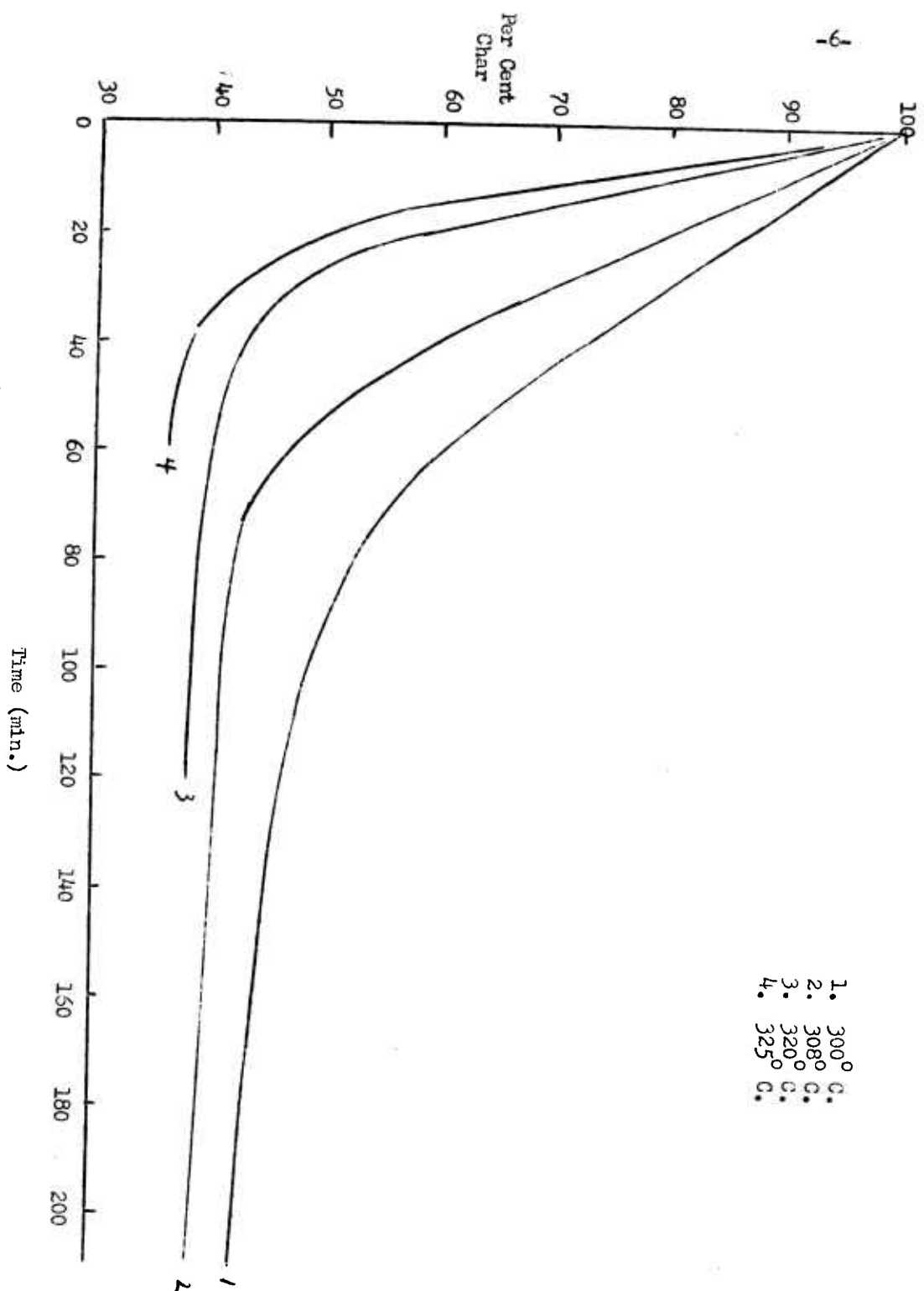


Figure 2. Variation of char with time in the pyrolysis of untreated 80 square cotton fabric

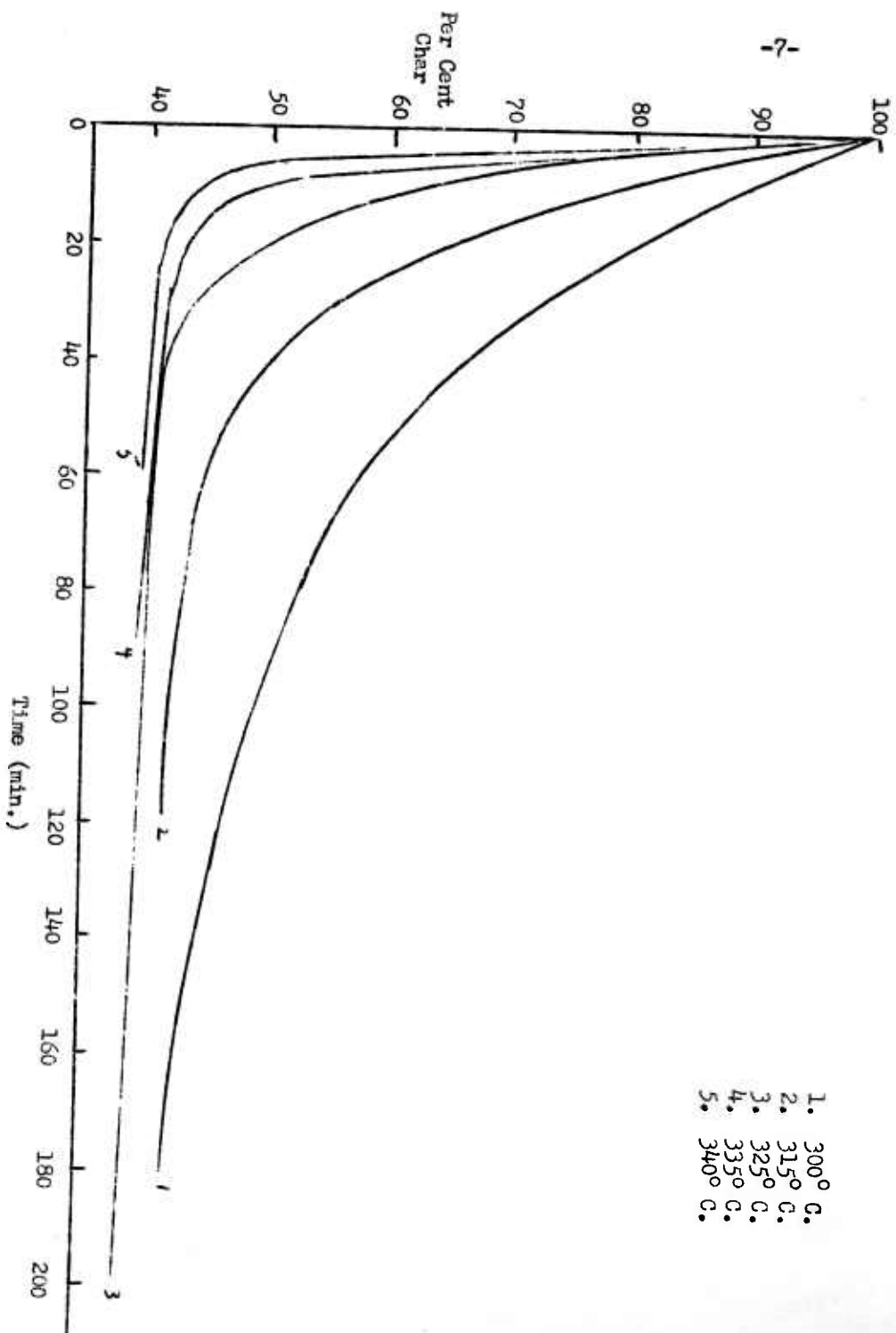


Figure 3. Variation of char with time in the pyrolysis of untreated linen fabric

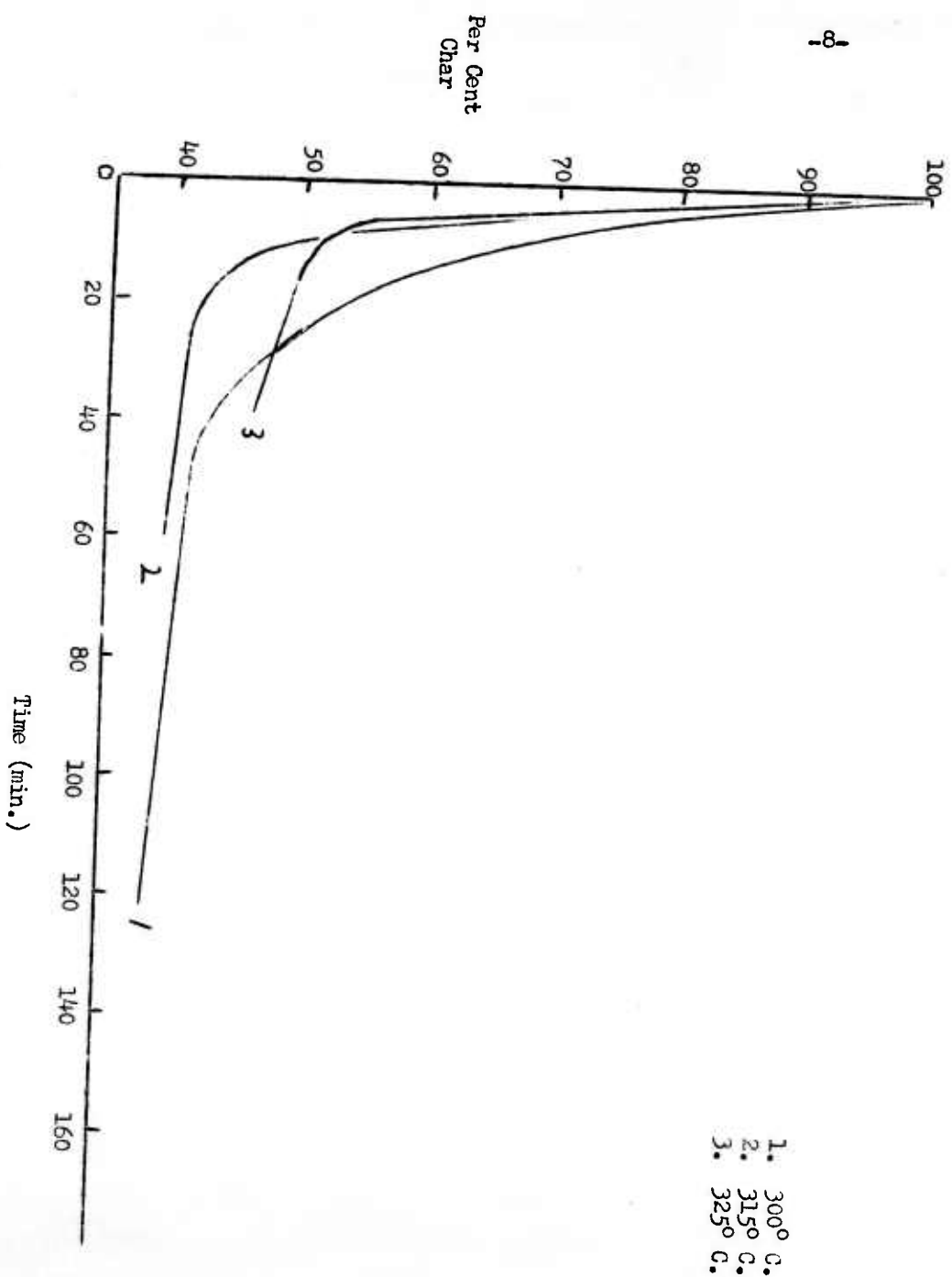


Figure 4. Variation of char with time in the pyrolysis of untreated rayon fabric

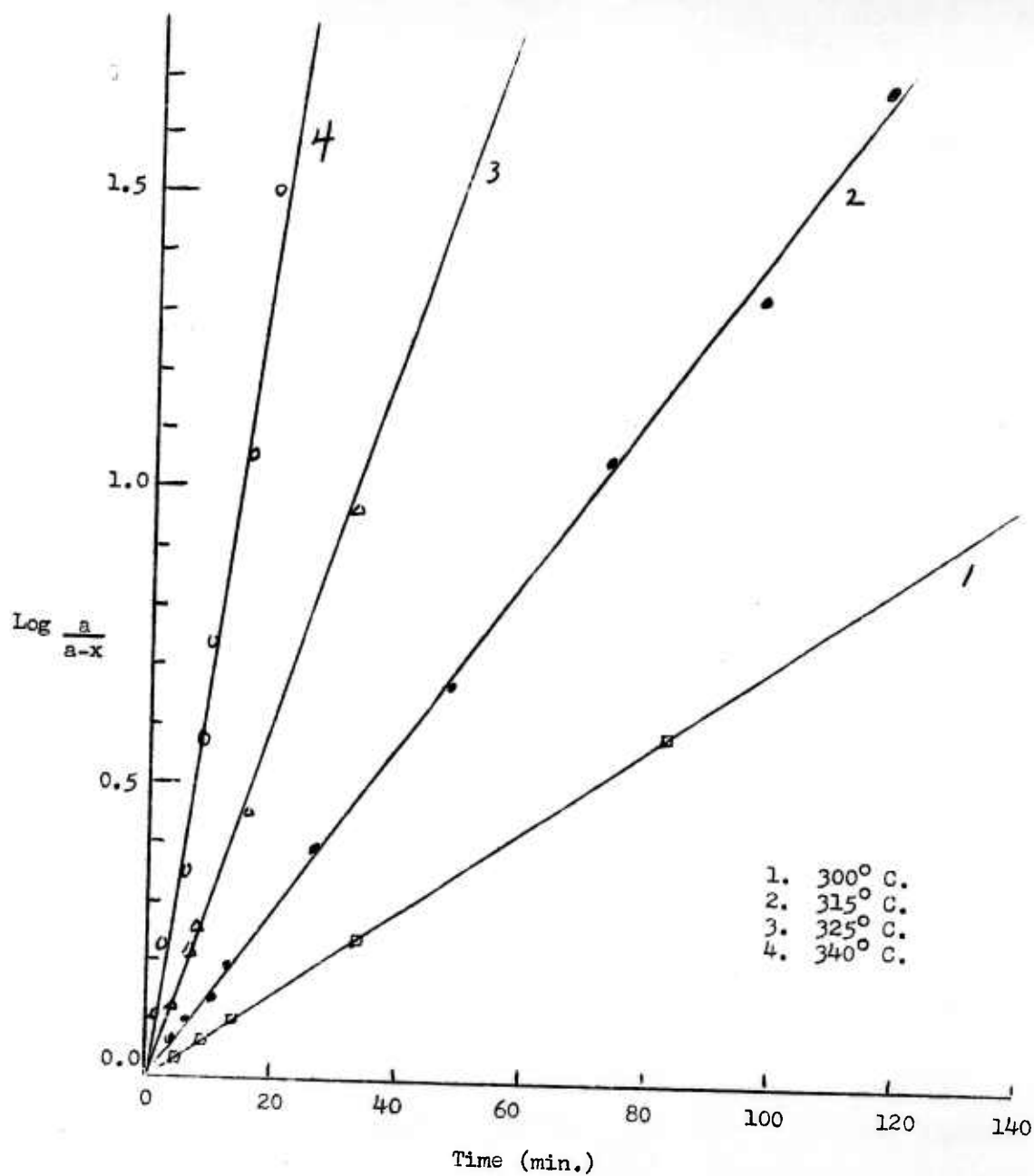


Figure 5. First-order pyrolysis of untreated cotton khaki fabric

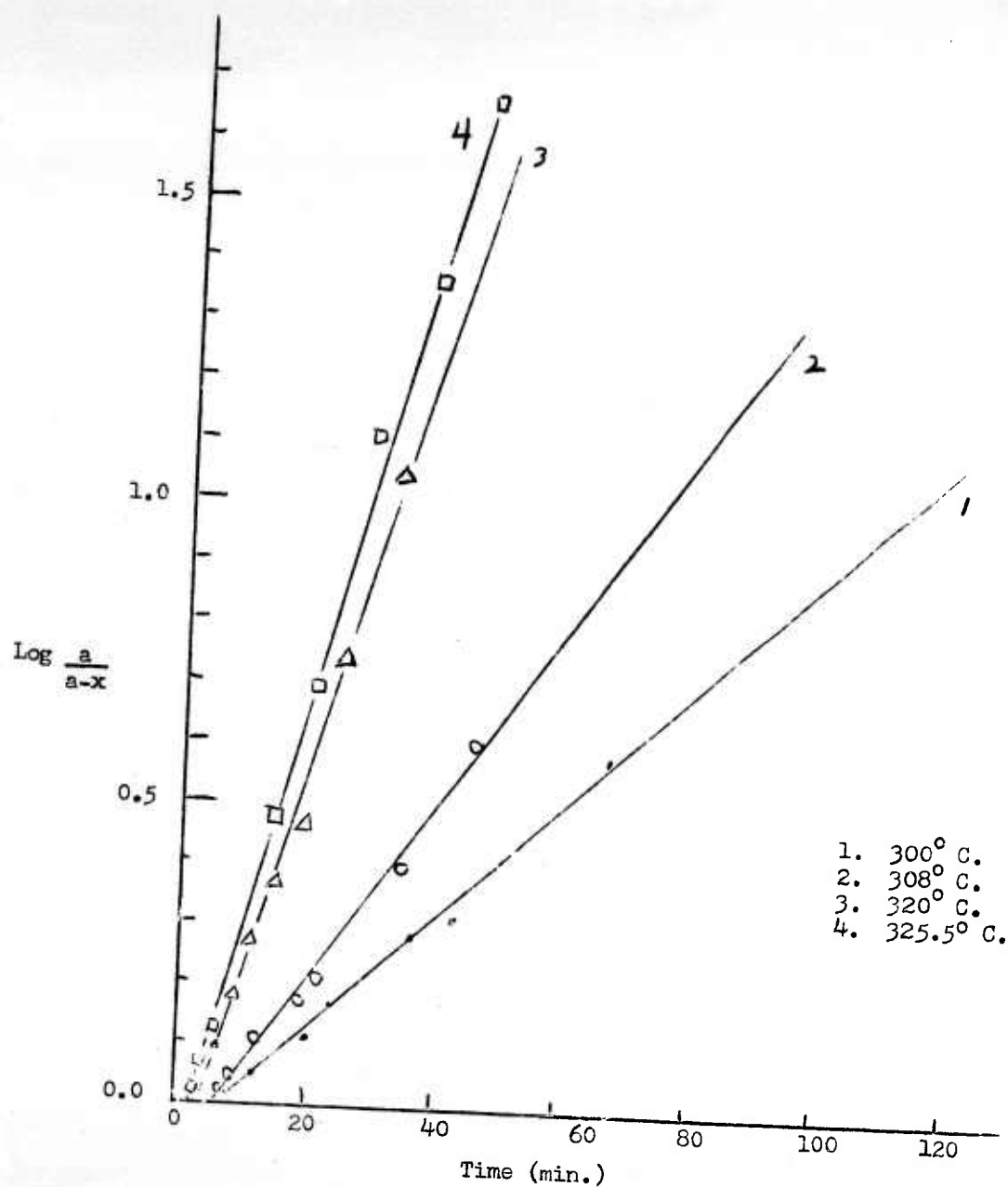


Figure 6. First-order pyrolysis of untreated 80 square cotton fabric

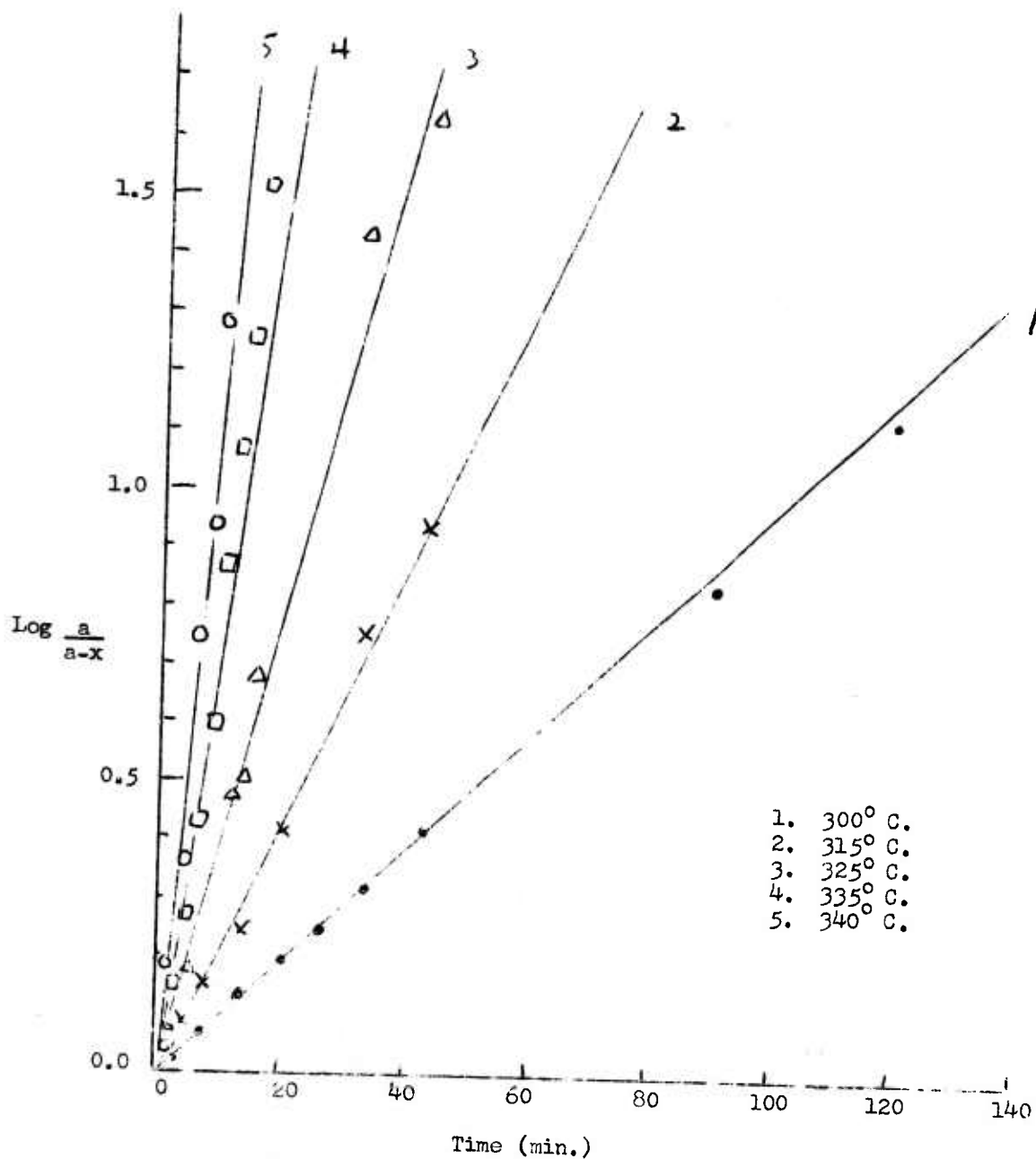


Figure 7. First-order pyrolysis of untreated linen fabric

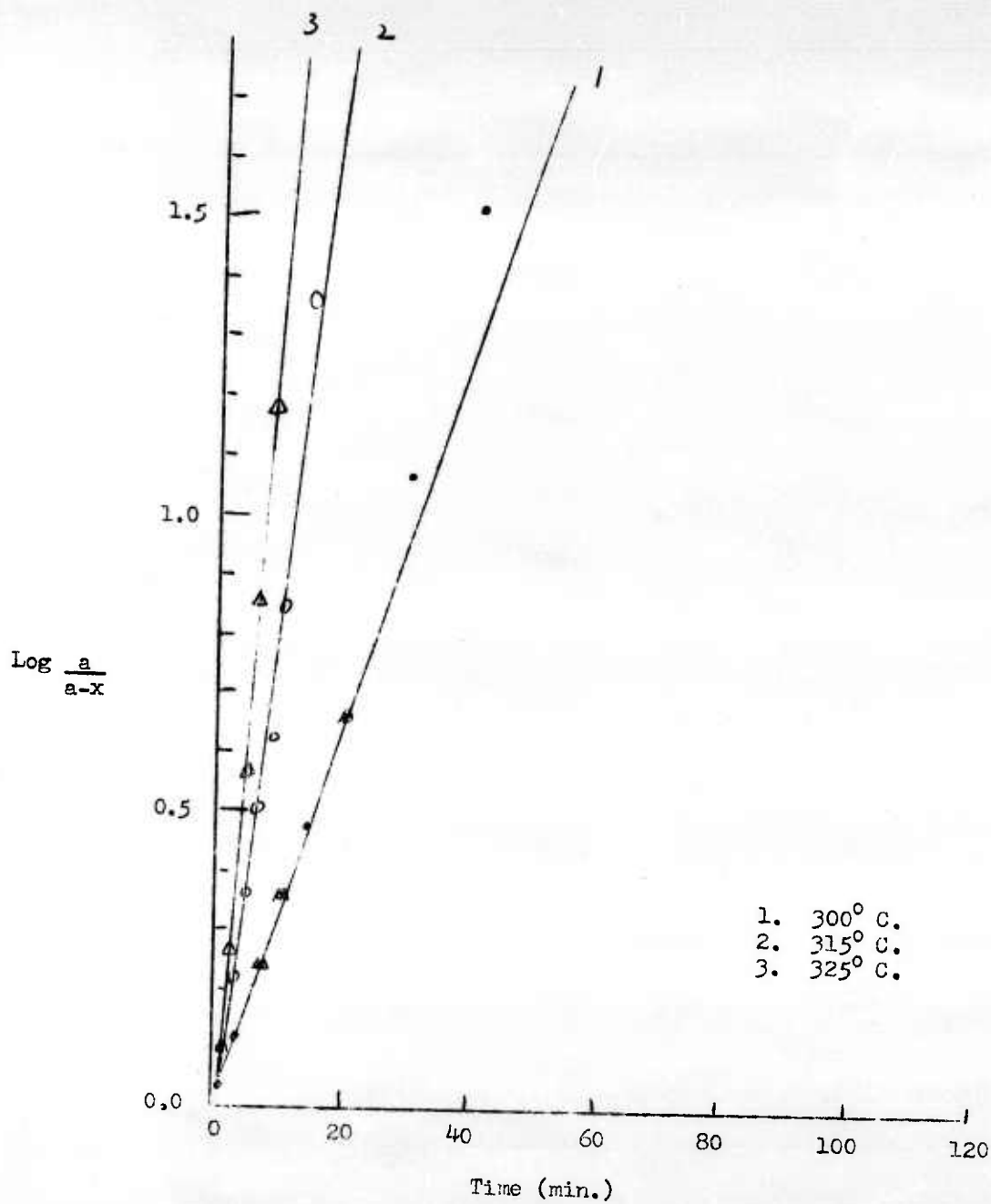


Figure 8. First-order pyrolysis of untreated rayon fabric

TABLE II

Activation Enthalpy (Energy) Observed in the Pyrolysis
of Some Untreated Cellulosic Fabrics

<u>Sample</u>	<u>ΔH^* (kcal.)</u>
Cotton khaki	43.4
80 Sq. cotton	40.8
Linen	41.2
Rayon	43.1

TABLE III

Specific Rate Constant (min.^{-1}) Observed in the
Pyrolysis of Treated Cotton Khaki Fabric
at Different Temperatures

Temperature ($^{\circ}\text{C.}$):	<u>260</u>	<u>270</u>	<u>280</u>	<u>290</u>	<u>300</u>
2.8% Na_2CO_3	.011	.018	.021	.030	
1.6% KClO_4				.020	.036
3% NaCl				.021	.034

Radiant Energy Decomposition of Cotton Fabric

An evaluation of the effect of radiant energy on untreated and variously treated cotton fabrics has been started. The apparatus for this study has been described previously⁷. The treatments were applied at this laboratory and at the Quartermaster Research & Development Laboratories. In Figures 9 and 10 are given the variation of per cent char with time for the samples studied. The decomposition was completed in an inert atmosphere of nitrogen.

The procedure, described previously¹, for measuring temperature behind the samples during exposure to radiant energy is under investigation. The apparatus consists of a one mil platinum-rhodium gold-palladium

thermocouple, incorporated within a Teflon mount. A rapid response recording potentiometer is used to record the e. m. f. produced at the hot junction of the thermocouple. At the present time the method has not been developed to give reproducible results.

Comparison of Radiant Energy Decomposition with Thermal Decomposition

of Untreated and Treated Cotton Fabrics. An important phase of the evaluation program is the comparison of char/tar ratios resulting from the pyrolytic decomposition of untreated and treated fabrics at different rates. Three different rates of decomposition were used as follows:

1. Slow furnace. The sample, contained in a constricted test tube, the upper part of which was packed with Pyrex glass wool, was placed in a furnace at room temperature in a position for the recovery of tars by downward distillation. A slightly reduced pressure was maintained (560-570 mm.). The furnace was heated to 400° C. (30 minutes), and the decomposition continued at that temperature for an additional 60 minutes.
2. Fast furnace. The apparatus and procedure for this method was as described except that the furnace was preheated to 400° C. before introduction of the sample.
3. Radiant energy. The use of radiant energy probably provided the greatest rate of incident energy for the decomposition. The experiments were completed using a flow of nitrogen in the cell in order to maintain pyrolytic conditions and increase the collection of tars in a Pyrex glass wool trap. As in the case of the furnace decomposition, the radiant energy experiments were carried out using an infinite time exposure to insure complete degradation.

The results obtained are listed in Table IV.

The results obtained indicate that as the rate of incident energy increases the amount of tar produced increases. A shorter time was required for the carbon black treated sample because the treatment reduced the amount of energy reflected from the sample.

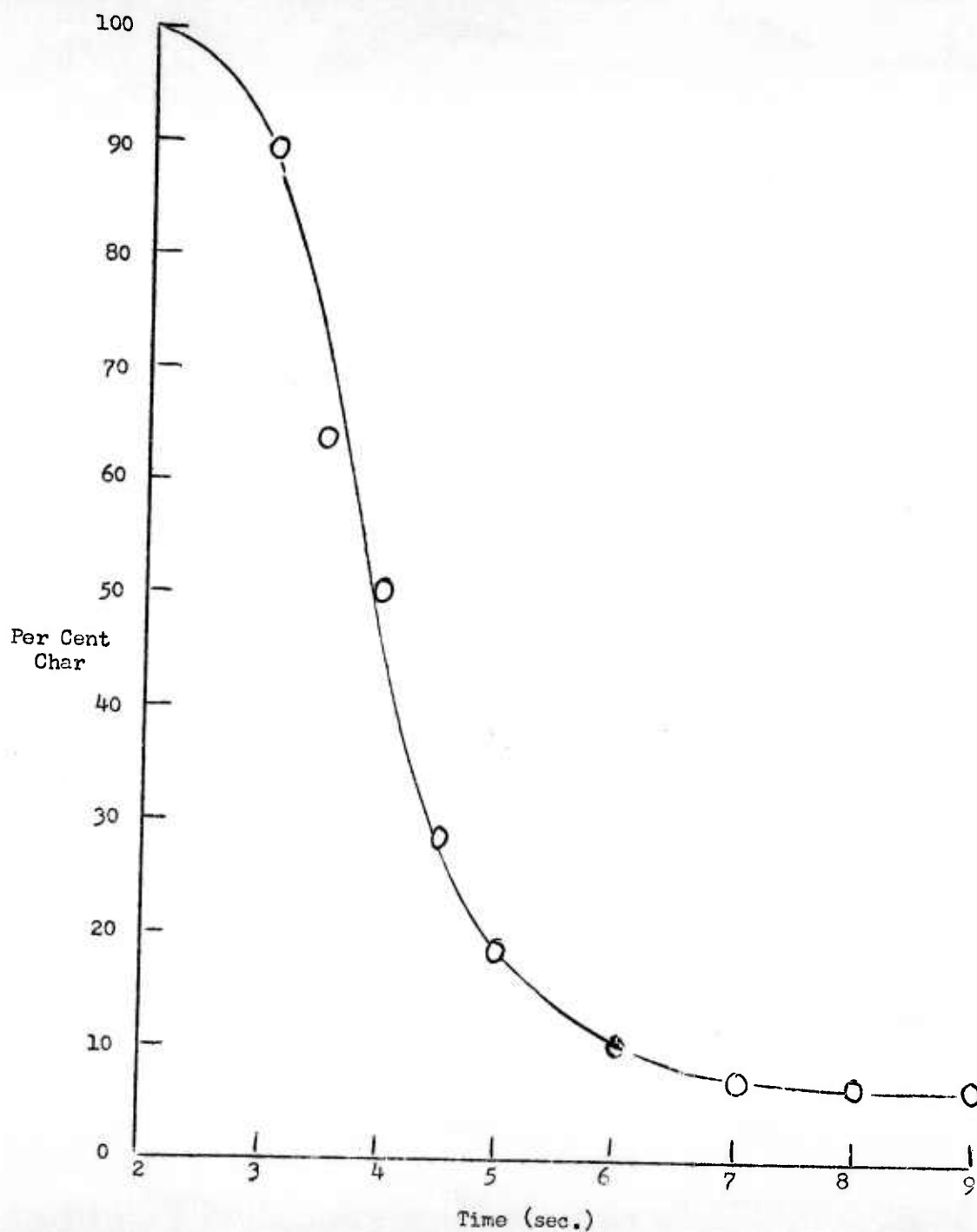


Figure 9. Variation of char with time in the radiant energy decomposition of untreated cotton sateen fabric, 8.5oz., OG-107, at an irradiance of $5.3 \text{ cal. cm.}^{-2} \text{ sec.}^{-1}$

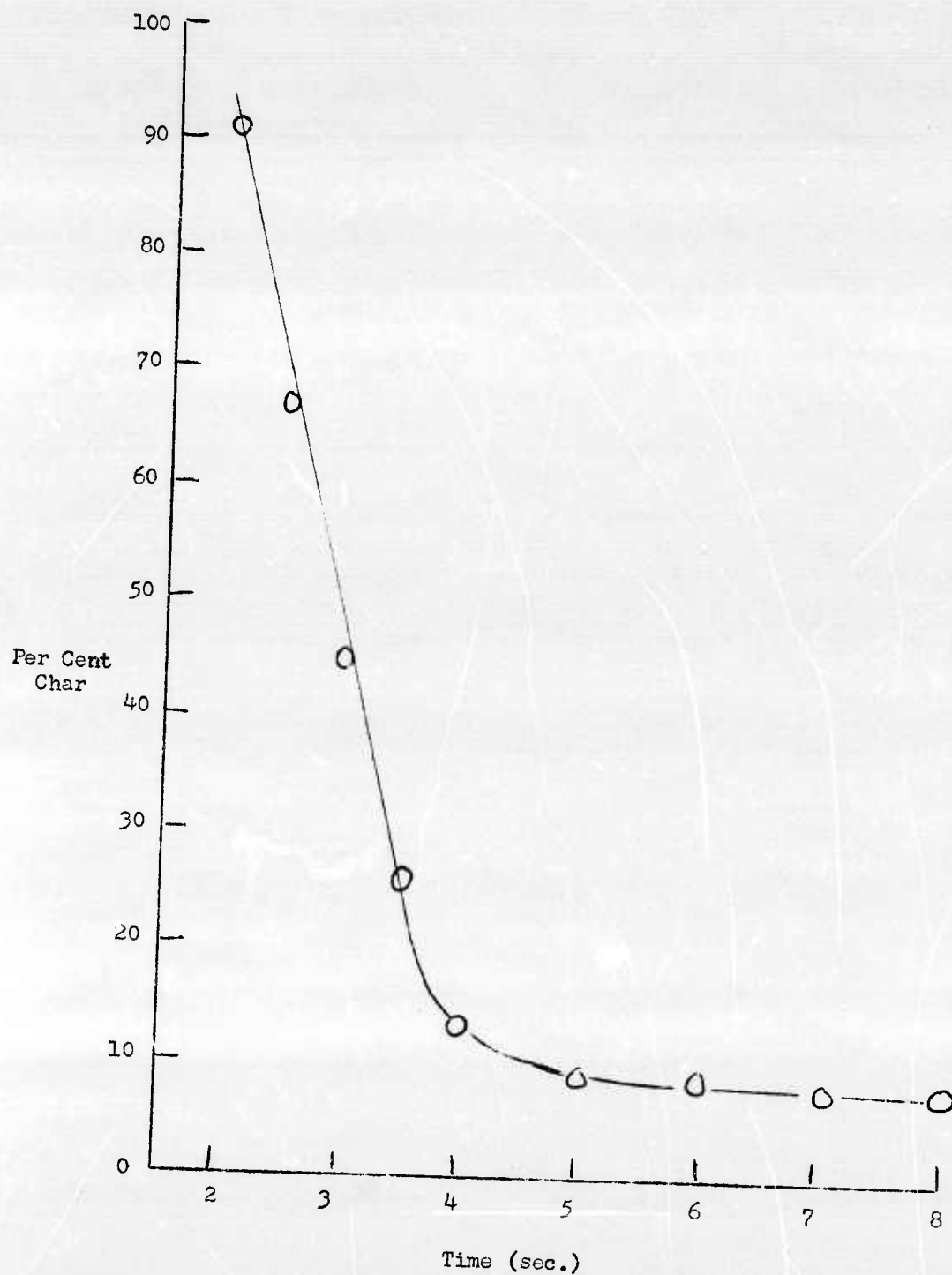


Figure 10. Variation of char with time in the radiant energy decomposition of cotton sateen fabric, 8.5 oz., CG-107, with 1% addition of carbon black, at an irradiance of $5.3 \text{ cal. cm.}^{-2} \text{ sec.}^{-1}$

TABLE IV
Comparison of Thermal and Radiant Energy
Decomposition of Cotton Fabric

Sample	% Char	Furnace Block Decomposition at 400° C.				Radiant Energy Decomposition (5.3 cal. cm ² Sec. -1)		
		Slow % Tar	Char/Tar ^a	% Char	Fast % Tar	Char/Tar ^a	% Char ^b	% Tar ^b Char/Tar ^a
Cotton khaki	21.8	39.7	0.562	17.8	47.1	0.352	7.9	42.6 0.184
Twill, 8.2 oz., untreated	22.2	38.6		17.6 18.1 18.1	49.2 54.3 52.5		8.5	44.9 (12 sec.)
Cotton khaki	21.6	41.0	0.529	18.2	46.5	0.387	7.4	46.7 0.163
Twill, 8.2 oz. 1% carbon black	21.7	41.0		17.9	46.9		8.3	47.4 (6 sec.)

^aThe char/tar ratio was calculated from the averages of the several experiments.
^bThe per cent of char and tar resulting from the radiant energy experiments was based on the decomposition of 25 samples.

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5. C. A. 44 7257f; 45, 6569 i, 8444b, 10191a. Abstracts of articles by M. I. Kabachnik, et al., (Acad. Sci. U. S. S. R., Moscow) Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1950, 39, 635; 1951, 185; Doklady Akad. Nauk S. S. S. R., 75, 219 (1950).
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